# Fast GC method for pesticides/PCBs in feed matrices by split injection GC-APCI-MS/MS

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## Background

in the past decade the method of choice for multi-residue analysis of pesticides has shifted from GC to LC. This is because (U)HPLC-MS/MS outperforms GC-EI-MS/MS in terms of speed and in many cases also sensitivity/selectivity and robustness. However, since not all pesticides are LC-MS amenable, a complementary GC analysis is required and hence there is a need for faster and better GC methods.

GC-APCI-MS/MS is one option to achieve this goal because:
- $M^{\cdot+}$ or $[M+H]^+$ is highly abundant and can be used as precursor ion resulting in improved sensitivity/selectivity
- The high sensitivity allows split injection which results in
  - no need for solvent trapping → high initial GC oven temperature
  - much less matrix onto the GC column
- Compatible with high carrier gas flow rates; combined with high initial GC oven temperature and high T-ramp = short run time

## Objective

- Optimization of split injection / fast gas chromatography
- Validation of fast method for analysis of (complex) feed materials

## Experimental

- Extraction: QuEChERS (acetate buffered, dSPE with PSA/C18)
- Final extract: 0.25 g/mL
- GC-MS/MS: 7890A (Agilent) – Xevo TQ-S (Waters)
- Injection: 1 µL split 1:10
- Carrier gas: helium
- Column: 0.25 mm ID, 0.25 µm Cl-Pesticides (Restek)
- Source: APCI (charge transfer conditions)

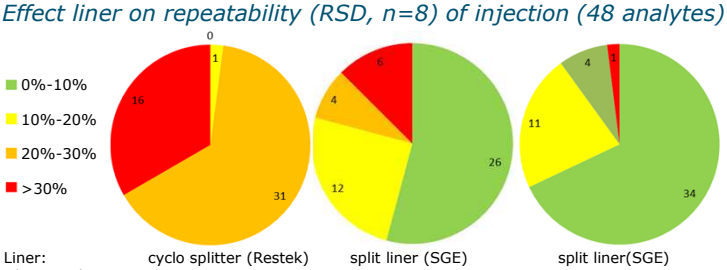
### *Validation set*

1 sample of each matrix (n=5): blank, spikes at 0.01 and 0.05 mg/kg

Wheat | Maize | Sunflower seed meal | Beet pulp | Yeast Concentrate

## Results

### *Effect liner on repeatability (RSD, n=8) of injection (48 analytes)*




| | | | |
|---|---|---|---|
| Liner: | cyclo splitter (Restek) | split liner (SGE) | split liner(SGE) |
| Glass wool: | no | yes | yes |
| Carrier/Split flow: | 2/20 mL/min | 2/20 mL/min | 6/60 mL/min |

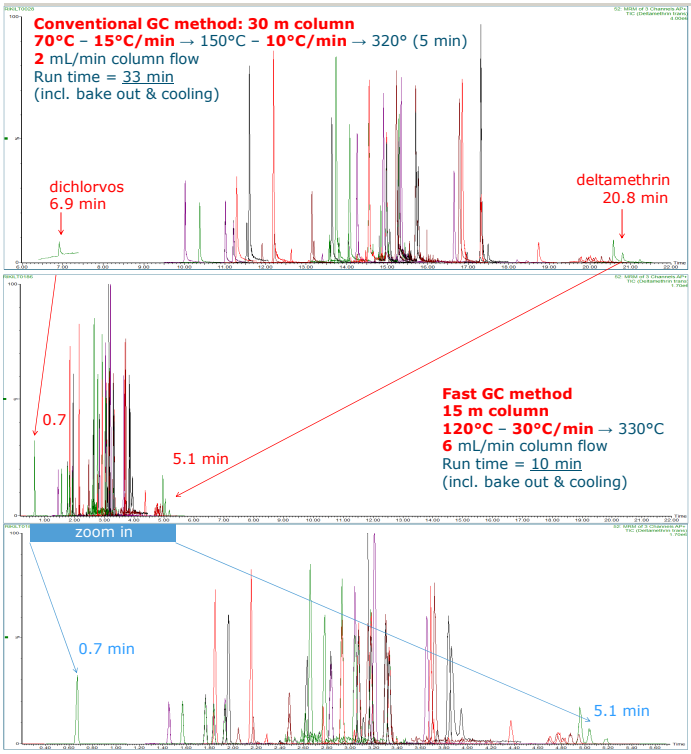



**Table 1.** Average recovery (%) and RSD (%) for each analyte in set of 5 different matrices (1-point calibration, standard addition to extract @ 0.05 mg/kg equivalent)

| Analyte | 0.01 mg/kg | 0.05 mg/kg | Analyte | 0.01 mg/kg | 0.05 mg/kg |
|---|---|---|---|---|---|
| Aldrin | 72 (12) | 87 (13) | Endrin | 89 (5) | 86 (10) |
| Bifenthrin | 81 (6) | 83 (5) | Fenitrothion | 90 (15) | 96 (2) |
| Bromopropylate | 90 (12) | 96 (17) | Fenvalerate | 89 (9) | 86 (2) |
| Chlordane cis- | 81 (17) | 93 (9) | Flucythrinate | 97 (11) | 92 (8) |
| Chlordane trans- | 89 (1) | 86 (14) | HCB | 77 (2) | 71 (14) |
| Chlorobenzilate | 93 (15) | 97 (8) | HCH alpha- | 98 (6) | 97 (11) |
| Chlorothalonil | 3 (74) | 24 (88) | HCH beta- | 94 (16) | 94 (10) |
| Chlorpyrifos-methyl | 108 (32) | 100 (14) | HCH gamma- | 96 (10) | 94 (7) |
| Cyfluthrin | 92 (12) | 95 (10) | Heptachlor | 83 (10) | 89 (10) |
| Cyhalothrin lambda- | 93 (10) | 91 (11) | Heptachlor epoxide | 94 (6) | 96 (11) |
| Cypermethrin | 99 (7) | 97 (3) | Methoxychlor | 97 (10) | 97 (7) |
| DDD o,p'- (TDE) | 88 (5) | 90 (7) | Oxychlordane | 107 (28) | 103 (12) |
| DDD p,p'- (TDE) | 86 (5) | 87 (12) | Parathion-ethyl | 100 (10) | 98 (21) |
| DDE o,p'- | 81 (5) | 82 (8) | Parathion-methyl | 96 (13) | 110 (14) |
| DDE p,p'- | 75 (5) | 76 (9) | PCB28 | 81 (11) | 76 (22) |
| DDT o,p'- | 79 (12) | 79 (12) | PCB52 | 79 (9) | 79 (1) |
| DDT p,p'- | 83 (12) | 83 (11) | PCB101 | 66 (19) | 69 (16) |
| Deltamethrin cis- | 91 (16) | 87 (9) | PCB138 | 64 (8) | 63 (16) |
| Dichlorvos | 94 (16) | 98 (12) | PCB153 | 56 (8) | 63 (20) |
| Dicloran | 96 (5) | 99 (11) | PCB180 | 54 (2) | 50 (16) |
| Dieldrin | 82 (18) | 93 (2) | Permethrin | 79 (55) | 92 (9) |
| Disulfoton | 70 (43) | 90 (43) | Procymidone | 92 (29) | 103 (15) |
| Endosulfan beta- | 85 (25) | 90 (23) | Tetramethrin | 100 (15) | 100 (5) |
| Endosulfan sulphate | 98 (9) | 96 (10) | Vinclozolin | 94 (10) | 104 (15) |

## Conclusions

- Liners with glass wool required for reliable split injection
- Run time reduced by factor 3 with only slight reduction of resolution
- Acceptable recoveries and RSDs for most of the analytes

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